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T DOCUMENTATION PAGE

1a. REI None	1b. RESTRICTIVE MARKINGS None
2a. SECURITY CLASSIFICATION AUTHORITY None	3. DISTRIBUTION/AVAILABILITY OF REPORT Unlimited
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE None	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report #2	5. MONITORING ORGANIZATION REPORT NUMBER(S) ONR N00014-87-K-0438
6a. NAME OF PERFORMING ORGANIZATION University of Arizona; 6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research
6c. ADDRESS (City, State, and ZIP Code) Department of Chemistry, University of Arizona, Tucson, AZ 85721	7b. ADDRESS (City, State, and ZIP Code) 800 North Quincy Avenue, Arlington, VA 222[illegible]
8a. NAME OF FUNDING/SPONSORING ORGANIZATION ONR; 8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
8c. ADDRESS (City, State, and ZIP Code) 800 N. Quincy Avenue, Arlington, VA 22217	10. SOURCE OF FUNDING NUMBERS: PROGRAM ELEMENT NO. / PROJECT NO. / TASK NO. / WORK UNIT ACCESSION NO

11. TITLE (Include Security Classification)

New Gem-Dicyanocyclobutane-Containing Hydroxyesters

12. PERSONAL AUTHOR(S)

Shoji Mori, Toyoji Kakuchi, Anne Buyle Padias, and H. K. Hall, Jr.

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Technical	FROM _____ TO _____		

16. SUPPLEMENTARY NOTATION

J. Polym. Sci., Polym. Chem. Ed.

17 COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

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beta

cyclobutanes, cyanogen, hydroxyl radicals, esters. (engn)

DTIC ELECTED 11 APR 1989 S C E

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION
22a. NAME OF RESPONSIBLE INDIVIDUAL H. K. Hall, Jr.	22b. TELEPHONE (Include Area Code) 602-621-6325; 22c. OFFICE SYMBOL

DD FORM 1473, 84 MAR 83 APR edition may be used until exhausted. All other editions are obsolete

SECURITY CLASSIFICATION OF THIS PAGE

89 4 10 213

Office of Naval Research

Contract N00014-87-K-0438

R&T Code 413j009

Technical Report No. 2

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by

Shoji Mori, Toyoji Kakuchi, Anne Buyle Padias, and H. K. Hall, Jr.

Submitted for Publication in

J. Polym. Sci., Polym. Chem. Ed.

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April 1, 1989

Contribution from the C. S. Marvel Laboratories
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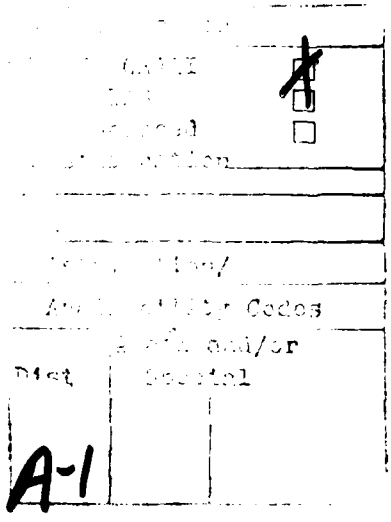


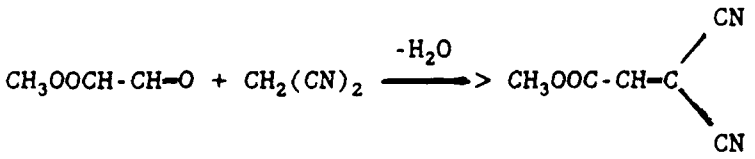
Abstract

Six new gem-dicyanocyclobutanes containing carbomethoxy and hydroxyl/acetoxy functions were synthesized by cycloaddition of the appropriate vinyl ethers or alkoxystyrenes to methyl β,β-dicyanoacrylate. They proved to be too thermally labile to allow polycondensation to potentially piezoelectric linear polyesters.

Introduction

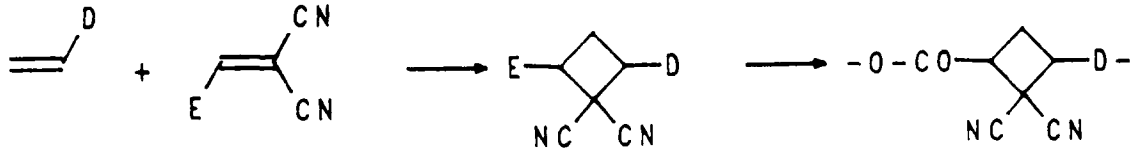
Multicyano polymers, particularly the copolymer of vinylidene cyanide and vinyl acetate, are of current interest as piezoelectric materials.[1] We have long been interested in cycloaddition reactions of multicyano olefins.[2] Using such reactions, we have now synthesized new cyano-containing monomers for possible polycondensations to potential new piezoelectric materials.

Methyl β,β-dicyanoacrylate (DCA) is readily available from Knoevenagel condensation of methyl glyoxylate with malononitrile.[3]



This electrophilic trisubstituted ethylene is very reactive in [2+2] cycloadditions with electron-rich olefins. The solvent was an important factor in these results.[4] Cyclobutane adduct formation with p-methoxystyrene was favored in methanol.

We have now carried out analogous cycloadditions using hydroxy or acetoxy-containing styrenes or vinyl ethers. We hoped to obtain hydroxy- or acetoxy-ester intermediates suitable for making dicyanocyclobutane-containing condensation polymers.



D = donor substituent: -OR or -Ar group

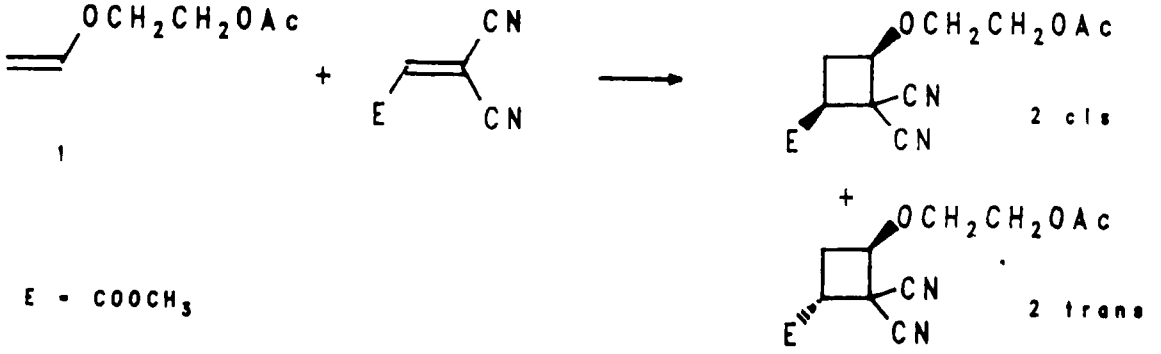
E = $COOCH_3$

Results

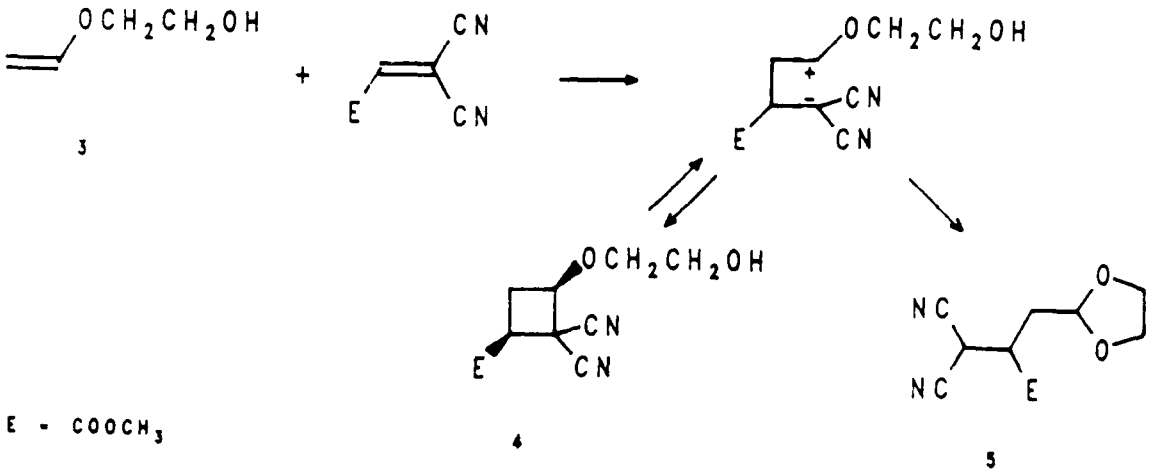
Three types of donor olefins, each containing a terminal hydroxy or acetoxy substituent, were used in the cycloadditions with methyl β,β-dicyanoacrylate: aliphatic vinyl ethers, aromatic vinyl ethers and p-alkoxy-substituted styrenes.

Cycloaddition with Acetoxyethyl or Hydroxyethyl Vinyl Ether

At -20°C for 20 hrs in tetrahydrofuran, the acetoxy derivative 1 with excess DCA gave largely cyclobutane 2 contaminated with oligomeric DCA. After purification by column chromatography, cyclobutane 2 was obtained as a cis-trans (60:40) mixture in 56% yield. The pure cis, and almost pure trans, isomers could be separated by further chromatography.

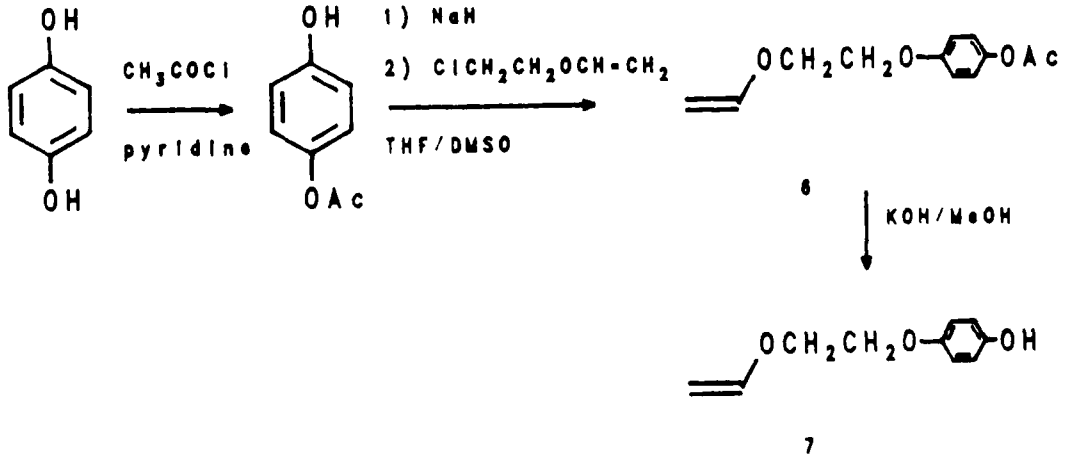


Under the same conditions, hydroxyethyl vinyl ether 3 led to a mixture of the cis isomer of the expected cyclobutane adduct 4 (42% yield) and the dioxolane 5. Upon attempted separation by column chromatography, the cyclobutane 4 completely rearranged to form the dioxolane adduct 5. This rearrangment occurs via the zwitterionic tetramethylene intermediate.

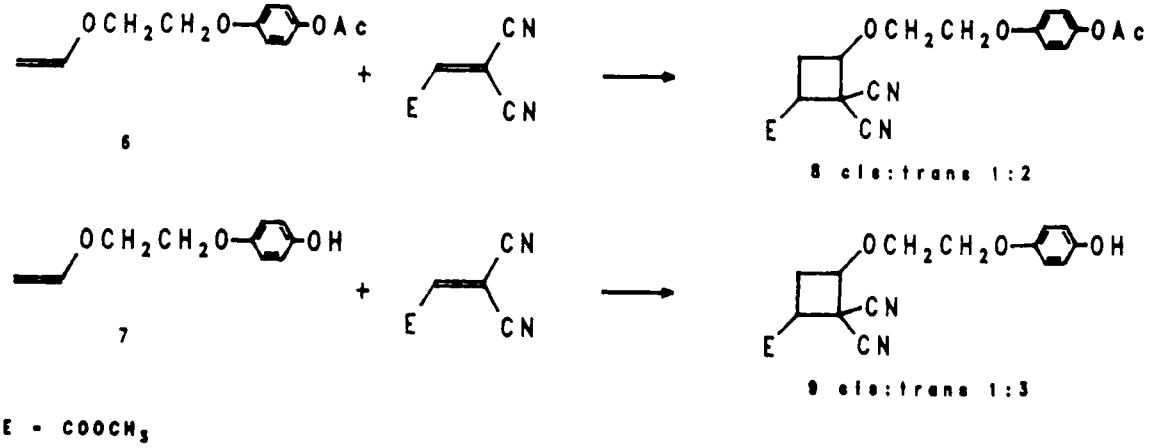


Cycloaddition with Aromatic-Containing Vinyl Ethers

The synthesis of the aromatic-containing substituted vinyl ethers 6 and 7 starts with the monoacetylation of hydroquinone, followed by reaction of β-chloroethyl vinyl ether with the remaining hydroxy function in basic conditions (53% yield). Deacetylation of 6 leads to the phenolic vinyl ether 7 in 85% yield.



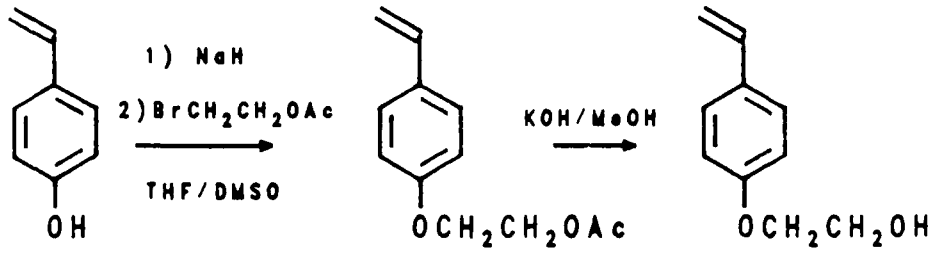
The cycloadditions of these vinyl ethers 6 and 7 with DCA were carried out as described above for the aliphatic vinyl ethers. The yields of cyclobutane 8 and 9 were 68% and 60%, respectively; cis-trans ratios were 1:2 and 1:3, respectively.



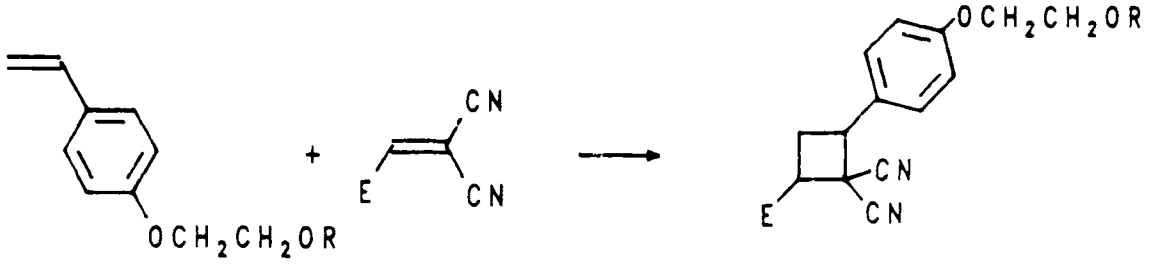
E = $COOCH_3$

Cycloaddition with p-Alkoxystyrenes

The p-alkoxystyrenes were synthesized by derivation of p-hydroxystyrene. Reaction of p-hydroxystyrene in basic conditions with β-bromoethyl acetate leads to p(β-acetoxyethoxy)styrene 10. Treatment with alkaline methanol leads to p-(β-hydroxyethoxy)styrene 11.



The cycloadditions with DCA proceeded most effectively in methanol. This is in agreement with the results obtained previously for p-methoxystyrene.[4] In other solvents, such as acetonitrile, dichloromethane, toluene or DMSO, complex mixture of the desired cyclobutane adducts, double Diels-Alder adducts and oligomeric products were obtained. In methanol, the cyclobutane adducts 12 and 13 from the p-acetoxy and the p-hydroxy derivatives, respectively, were obtained in 70% and 64% yield.



10 R = $COCH_3$

11 R = H

12 R = $COCH_3$

13 R = H

Stability of Cyclobutane Cycloadducts

Most of the cyclobutanes were stable at room temperature. However, on storage without special precautions, the NMR spectrum of 13 showed complete disappearance of cyclobutane signals, and in several other cases, aldehyde protons appeared, corresponding to hydrolysis.

Even mild heating to ~40°C, gave thermal decomposition of any of the cyclobutanes. The acetates were generally more stable than the alcohols.

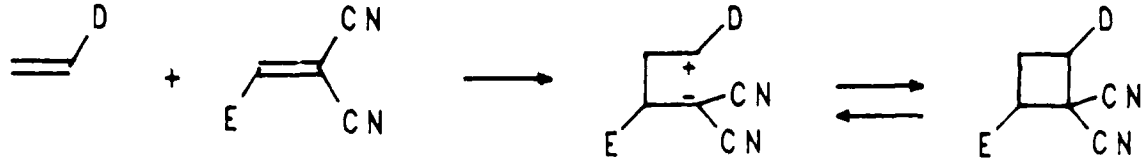
Attempted Polycondensation

We have tried to polymerize the hydroxy ester monomers using the standard thermal polycondensation method. However, even as low as 100°C, decomposition was much too extensive.

We tried to obtain the corresponding carboxy monomers to use in low-temperature polycondensations.[6,7] However, under the polar saponification conditions, the cyclobutanes underwent ring opening to unidentified products. When in one case we obtained a carboxylic acid, it proved to be unstable and isomerized to a lactone derivative.

Discussion

Facile cycloadditions of aliphatic vinyl ethers, aromatic vinyl ethers, and p-alkoxystyrenes to methyl β,β-dicyanoacrylate gave good yields of gem-dicyanocyclobutanes. The reactions proceeded through intermediate tetramethylene zwitterions in the case of the vinyl ether cycloadducts[5] or highly polar diradicals for the styrene derivatives.[4]



E = $COOCH_3$

D = donor substituent

However, the ease of formation of the tetramethylenes proved to be a two-edged sword. The cyclobutanes reverted to the tetramethylenes under very mild conditions. Accordingly, any polycondensations involving ester interchange, which generally involve heating with catalysts above 100°C, were out of the question.

Low temperature polymerizations of aromatic hydroxyacids involving the use of phosphorus coupling reagents, are known.[6,7] Accordingly, we attempted

to saponify the carbomethoxycyclobutanes to the corresponding acids. However, the polar saponification conditions also favored ionization of the cyclobutane back to the tetramethylenes.

We conclude that the proposed route to gem-dicyanocyclobutane polyesters will not be viable.

Experimental

Instrumentation. ^{1}H and ^{13}C NMR spectra were recorded on a 250-MHz WM-250 Bruker spectrometer. IR spectra were measured on a Perkin-Elmer 983 infrared spectrometer. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

Reactants. Methyl 3,3-dicyanoacrylate was synthesized by a Knoevenagel reaction of methyl glyoxylate and malononitrile.[3] 2-Vinyloxyethyl acetate 1 was synthesized according to Higashimura's procedure.[8] 2-Vinyloxyethanol 3 was obtained from hydrolysis of 1 in a potassium hydroxide-methanol (66-68°C/18mm Hg).

Acetoxyphenoxyethyl Vinyl Ether 6. To a flask containing p-hydroxyphenyl acetate (10g, 66 mmol) in THF (20 ml) was added a suspension of sodium hydride (1.9g, 79 mmol) in THF (10 ml) at room temperature. To this stirred mixture was added a solution of β-chloroethyl vinyl ether (Aldrich) (8.4g, 79 mmol) in dimethyl sulfoxide (10 ml) at room temperature. The reaction mixture stirred at 40°C for 20 hrs and then diluted with water and dichloromethane. The dichloromethane was washed with sodium hydroxide solution and water, dried, and recrystallized from methanol to give 6 (7.8g, 53%, m.p. 42-45°C). ^{1}H-NMR ($CDCl_3$) 7.00 and 6.91 (2d, 4H, phenyl), 6.54 (q, 1H, =CH), 4.27-4.0 (m, 6H, CH_2CH_2 and $-CH_2$) 2.27 (s, 3H, CH_3).

^{13}C-NMR ($CDCl_3$) 169.8, 156.3, 151.6, 145.5, 122.3, 115.3, 87.1, 67.8, 66.3, 21.0.

IR (KBr): 2933, 1753, 1620, 1540, 1220, 1197, 979, 909, 852, 838 cm^{-1}.

Chem Anal: Calcd. C,64.85; H, 6.35; Found C,64.51; H, 6.45

p-(Hydroxyphenoxyethyl Vinyl Ether 7. Ester **6** (5.6g, 25 mmol) in methanol (30 ml) was stirred with potassium hydroxide (0.1g) at room temperature for 24 hrs. After neutralization with Dry Ice, solvent was removed under vacuum. The crude product was recrystallized from methanol to provide phenol 7 (3.9g, yield 85%) as a white crystal, m.p. 81~81°C.

^{1}H-NMR ($CDCl_3$) 6.82 and 6.75 (2d, 4H, phenyl), 6.55 (q, 1H, =CH), 4.57 (s,1H, OH), 4.28~4.01 (m, 6H, CH_2CH_2 and $=CH_2$).

^{13}C-NMR ($CDCl_3$) 157.3, 152.6, 149.9, 132.2, 116.1, 89.5, 69.8, 66.4.

IR (KBr): 3385, 2929, 1619, 1513, 1452, 1238, 1203, 986, 828, 758 cm^{-1}.

Chem Anal: Calcd. C, 66.65; H, 6.71, Found: C, 65.86; H, 6.42.

p-(β-Acetoxyethoxy)styrene 10. Ester **10** was synthesized by the same procedure as **6** from p-hydroxystyrene (8g, 67 mmol) and 2-bromoethyl acetate (11g, 66 mmol) in 85% yield after distillation (115~120°C/0.5 mm Hg).

p-(2-Hydroxyethoxy)styrene (11). Alcohol **11** was obtained from hydrolysis of ester **10** by the same procedure of **7**.

General Procedure for Synthesis of Cyclobutanes. To a flask containing methyl β,β-dicyanoacrylate in THF was added dropwise electron-rich olefin in THF at -20°C under nitrogen atmosphere. After the reaction mixture was stirred at room temperature for 12 hrs, solvent was removed under vacuum. The crude product was purified by low-pressure column chromatography on silica gel (Merck, 60Å, 230-400 mesh). The cyclobutane adducts in this work are oils because of the long chain donor substituent. In contrast to the

p-methoxystyrene-DCA cyclobutane,[4] which was crystalline, these oils have to be purified by extensive column chromatography.

1-(β-Acetoxyethoxy)-2,2-dicyano-3-carbomethoxy-cyclobutane 2. Reaction of 2-vinyloxyethyl acetate 1 (3.9g, 14.6 mmol) and methyl β,β-dicyanoacrylate (4.0g, 29.4 mmol) in THF yield cyclobutane 2 (56%) as a pale yellow oil after purification by column chromatography (dichloromethane). Separation by a second column chromatography run provided cis and trans isomers of 2.

^{1}H-NMR ($CDCl_3$) 4.71 (2t, 1H,J=4.0Hz and J=10.0Hz), 4.31-4.26 and 3.91-3.81 (2m, 4H), 3.86 (s, 3H) 3.60 (q, 1H), 2.82 (2q, 1H, J=7.9Hz), 2.64 (2q, 1H, J=11.9Hz).

^{13}C-NMR ($CDCl_3$) 170.6, 168.9, 112.4, 111.9, 78.3, 68.9, 62.6, 53.3, 40.2, 36.1, 30.9, 20.7 ppm.

IR (KBr): 2957, 2247, 1742, 1438, 1365, 1235, 1181, 1148, 1061 cm^{-1}.

Chem Anal: Calcd. C,54.13; H, 5.30; N,10.51, Found: C,53.89; H, 5.31; N, 10.54.

1-(β-Hydroxyethoxy)-2,2-dicyano-3-carbomethoxy-cyclobutane 4. Cyclobutane 4 was obtained from 2-vinyloxyethanol 2 (3.8g, 43 mmol) and methyl β,β-dicyanoacrylate (7g, 51 mmol) in THF as a pale yellow oil in 42% yield. After attempted purification by low-pressure column chromatography (dichloromethane-ether, 9:1), the rearranged dioxolane derivative 5 was obtained as the only product.

Cyclobutane 4: ^{1}H-NMR ($CDCl_3$) 4.73 (t, 1H), 4.08-3.09 (m, 4H), 3.83 (s,3H), 3.60 (q, 1H) 2.84 (q,H), 2.66 (q, H) ppm.

Rearranged product[5]: ^{1}H-NMR ($CDCl_3$) 5.00 (t, 1H, J=3.6Hz), 4.51 (d, 1H, J=6.7Hz) 4.05~3.85 (m, 4H), 3.84 (s,3H), 3.28 (m, 1H), 2.43 (2q, 1H), 2.25 (2q, 1H).

^{13}C-NMR ($CDCl_3$) 169.7, 111.8, 101.3, 65.1, 64.9, 53.2, 41.2, 31.9, 24.5.

IR (KBr) 2956, 2902, 2257, 1737, 1438, 1398, 1213, 1141, 1093, 1022, 946.

Chem Anal: Calcd. C, 53.57; H, 5.39; N, 12.50 Found: C,53.34; H, 5.29; N, 12.59.

1-[β-(p-Acetoxyphenoxy)ethoxy]-2,2-dicyano-3-carbomethoxycyclobutane 8

Cyclobutane 8 was obtained from vinyl ether 6 (2.7g, 12.1 mmol) and methyl β,β-dicyanoacrylate (2.5g, 18.2 mmol) in THF as a yellow oil in 68% yield after purification of low-pressure column chromatography (dichloromethane-ether, 95:5).

^{1}H-NMR ($CDCl_3$) 7.02 and 6.94 (dd, 4H) 4.81 (2t, 1H, J=4.0Hz and 10.0Hz), 4.21~4.00 (m, 4H) 3.94 (s, 3H), 3.58 (q, 1H) 2.84 (2q, 1H, J=7.9Hz), 2.63 (2q, 1H, J=11.9Hz).

^{13}C-NMR ($CDCl_3$) 169.8, 169.0, 160.5, 147.4, 122.4, 115.3, 78.9, 69.8, 67.4, 53.7, 53.3, 40.4, 37.1, 31.1, 21.0.

IR (KBr): 3073, 2956, 2247, 1732, 1614, 1505, 1436, 1339, 1192, 908, 844.

1-[β-(p-Hydroxyphenoxy)ethoxy]-2,2-dicyano-3-carbomethoxycyclobutane 9.

Cyclobutane 9 was obtained from p-(β-vinyloxyethoxy)phenol 7 (3.0g, 16.6 mmol) and methyl β,β-dicyanoacrylate (3.4g, 25 mmol) in THF as a yellow oil in 60% yield after purification of low-pressure column chromatography (dichloromethane-ether, 85:15).

^{1}H-NMR ($CDCl_3$) 6.74 (q, 4H), 6.16 (br S, 1H), 4.79 (t, 1H, J=7.9Hz), 4.15~3.97

(m, 4H), 3.59 (q, 1H), 2.84 (2q, 1H, J=4.0Hz and J=11.9Hz) 2.63 (2q, 1H, J=10.0 Hz).

^{13}C-NMR ($CDCl_3$ 169.0, 151.9, 150.0, 115.8, 115.6, 112.5, 112.1, 78.7, 69.9, 67.5, 53.2, 40.1, 37.0, 31.0.

IR (KBr): 3454, 2954, 2249, 1737, 1650, 1510, 1438, 1356, 1213, 829, 754.

1-[p-(β-Acetoxyethoxy)phenyl]-2,2-dicyano-3-carbomethoxycyclobutane 12.

Cyclobutane 12 was obtained from p-(β-acetoxyethoxy)styrene 10 (3.8g, 18.4 mmol) and methyl β,β-dicyanoacrylate (3.8g, 27.6 mmol) in methanol as a yellow oil in 70% yield after purification by low-pressure column chromatography (dichloromethane-ether, 9:1).

^{1}H-NMR ($CDCl_3$) 7.27 and 6.97 (2d, 4H) 4.41 and 4.20 (2t, 4H), 4.17 (2d, 1H, J=11.3Hz and J=6.3 Hz) 3.87 (s, 3H), 3.73 (q, 1H, J=11.0Hz), 3.00 (q, 1H, J=11.3Hz) 2.93~2.84 (m, 2H, J=11.3Hz, and J=8.7Hz), 2.10 (s, 3H).

^{13}C-NMR ($CDCl_3$) 170.9, 167.8, 128.8, 126.3, 115.8, 114.4, 65.9, 62.3, 53.3, 47.6, 46.3, 43.7, 42.8, 38.1, 26.1, 25.9, 20.8.

IR (KBr): 2955, 2247, 1739, 1609, 1514, 1437, 1375, 1236, 1058, 834.

Chem Anal: Calcd. C,63.15; H, 5.30; N, 8.13; Found C,62.45, H, 5.20; N, 8.26.

1-[p-(β-Hydroxyethoxy)phenyl]-2,2-dicyano-3-carbomethoxy-cyclobutane 13.

Cyclobutane 13 was obtained from p-(β-hydroxyethoxy)styrene 11 (5.3g, 32.3 mmol) and methyl β,β-dicyanoacrylate (6.6g, 48.4 mmol) in methanol as a yellow oil in 64% yield after purification by low-pressure column chromatography (dichloromethane-ether, 8:2).

^{1}H-NMR ($CDCl_3$) 7.27 and 6.98 (2d, 4H) 4.10~4.06 (m, 3H J=11.4Hz and J=6.3Hz), 3.97 (t, 2H), 3.86 (s, $3H_3$), 3.74 (t, 1H, J=11.0Hz), 3.00 (q, 1H, J=11.4Hz), 2.93~2.84 (m, 1H, J=8.6Hz), 2.17 (br s, 1H.

^{13}C-NMR ($CDCl_3$) 167.8, 128.7, 128.5, 126.1, 114.9, 114.3, 69.1, 61.2, 53.2, 53.0, 46.1, 42.8, 38.0, 26.0, 25.9.

IR (KBr): 3532, 2953, 2248, 1742, 1609, 1514, 1254, 1078, 1046, 834.

Chem Anal: Calcd. C, 63.99; H, 5.37; N, 9.33; Found: C,63.17, H, 5.32; N, 9.26.

Acknowledgement: The authors are indebted to the Office of Naval Research for partial financial support. A gift of p-hydroxystyrene from Dr. Lan Shan of Hoechst-Celanese, Corpus Christi, Texas, is also gratefully acknowledged.

References

1. Miyata, S.; Yoshikaza, M.; Tasaka, S.; Ko, M. Polym. J. 1980, 12, 857.

2. Hall, H. K. Jr. Angew. Chem. Int. Ed. Engl. 1983, 22, 440.

3. Hall, H. K. Jr.; Sentman, R.C. J. Org. Chem. 1982, 47, 4572.

4. Padias, A.B.; Hall, H. K. Jr. J. Org. Chem. 1987, 52, 4536.

5. Huisgen, R. Acc. Chem. Res. 1977, 10, 117.

6a. Higashi, F., Yamada, Y., and Hoshino, A. J. Polym. Sci. Polym. Chem. Ed., 1984, 22, 2181.

6b. Higashi, F., Takahashi, I. and Akiyama, N J. J. Polym. Sci. Polym. Chem. Ed., 1984, 22, 3607.

7. Yasuda, S., Wu, G.C., Tanaka, H., Sanui, K. and Ogata, N. J. Polym. Sci. Polym. Chem. Ed., 1983, 21, 2609.

8. Minoda, M., Sawamoto, M. and Higashimura, T. Polym. Bull., 1987, 17, 107.